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LETTER TO THE EDITOR

Observation of a flocculation to gel–sol scaling crossover in two-dimensional colloidal aggregation

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Abstract. The pair correlation function of a large connected cluster, formed during the irreversible aggregation of a two-dimensional distribution of colloidal microspheres, shows a distinct crossover from flocculation to gel-sol scaling behaviour consistent with kinetic clustering of cluster model predictions. Smaller isolated clusters arising out of the same aggregation even have lower than expected fractal dimensions, suggesting the influence of anisotropic interactions.

In a recent letter, Hurd and Schaefer [1] reported results from measurements of the fractal dimension and mass distribution of clusters formed by irreversible aggregation of colloidal silica microspheres confined to an air-water interface. They made direct microscope observations of the clustering process and determined a value for the fractal dimension, $D_F = 1.20 \pm 0.15$, from plots of the cluster radius of gyration, R_G, against mass, extracted from photomicrographs of the latter stage clusters. The observed cluster mass distribution was consistent with kinetic clustering of clusters [2] (KCC) model predictions, while the low fractal dimension apparently reflects the influence of anisotropic interactions [1, 3].

Colloidal particle monolayers (CPM) of this class may prove to be valuable as prototype experimental systems in studies of 2D aggregation kinetics. The particles are trapped at a flat air-water interface by surface tension forces. Surface energy potential well depths are orders of magnitude greater than kT, ensuring the rigorous two-dimensionality of CPM. Aggregation of charged CPM can be triggered by subsequent electrolytic 'poisoning' of the water supporting the monolayer or by dispersing the microspheres on salted water, the method used by Hurd and Schaefer. In either case the effect is to sharply reduce the strength of the repulsive, largely electric-dipolar, interaction between microspheres, enabling particles with sufficient kinetic energy to approach closely enough to bind via attractive van der Waals forces. CPM comprised of particles larger than 0.1 μm diameter can be observed directly using a microscope. Because they can be studied at the individual particle 'level' without the ambiguities arising from the effects of occlusion, studies of aggregating CPM can yield the same statistical information provided by computer simulations.

In our experiments, disperse CPM are first formed on the surface of ultraclean water contained in a trough mounted in a thermal isolation chamber and fixed to the viewing stage of a microscope. Once aggregation is induced, video records of the particle distribution within the microscope field of view are stored by a VCR, until clustering stops. Finally, digitised images of selected frames which span the collapse 'history' are subjected to computer analysis.

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A sample CPM is prepared by carefully applying a drop of a monodisperse suspension of microspheres in methanol to the surface of 18.3 MΩ cm water within the trough; the drop quickly spreads, distributing the spheres uniformly over the entire surface. We use either polystyrene or polyvinyltoluene spheres in the 0.2–2.0 μm diameter size range, with either sulphonate or carboxyl surface head groups. For spheres within the above size range, and for separations exceeding the Debye length, dipolar forces dominate. Under these conditions, sulphonated CPM samples form defect-sparse 2D triangular lattice crystals covering the surface, with overall stability enforced by the trough boundary; equivalent carboxyl surface samples are liquid or even gas-like. This difference arises because SO_4H ionises more efficiently than COOH in water, increasing the relative dipole moment of a sulphonated microsphere. If the sample is established within a Langmuir trough, its number density can be varied smoothly and reversibly, over more than two orders of magnitude [4], by changing the position of the movable barrier. This enables us to form a sample, and then to precisely adjust its density to a preselected value.

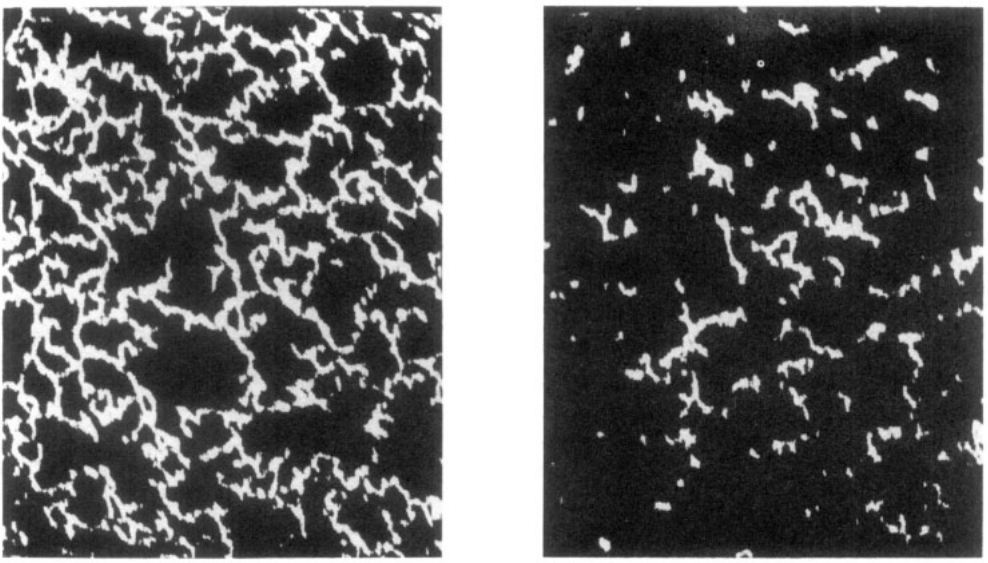
Once the initial CPM has stabilised, aggregation is triggered by carefully adding a concentrated salt or acid solution to the water; this shortens the Debye length with a consequent dramatic reduction in the strength of the repulsive interparticle forces. While this method induces clustering in carboxyl sphere CPM, we find it necessary to remove the cover of the isolation chamber to start a sulphonate CPM aggregating. Apparently thermal currents assist in driving the spheres through the still substantial repulsive barrier into the attractive van der Waals regime where clustering occurs.

In this letter we report measurements of fractal scale invariance in a single 'giant' connected cluster and in smaller isolated clusters, produced during the irreversible aggregation of a CPM.

The initial CPM was formed by depositing a suspension of 0.38 μm diameter polystyrene microspheres within a 3.5 cm diameter circular trough. Once stabilised, the system resembled a 2D gas of monomers with a small number of dimers and trimers, and was inhomogeneous, being made up of large regions (10^5–10^7 particles) of differing average number density, ρ_0 ($0.1 \leqslant \rho_0 \leqslant 0.2$). Aggregation was induced by injecting HCl into the water.

After the HCl was added, active clustering ceased within several hours. Then, VCR frames of the connected (figure 1(*a*)) and isolated (figure 1(*b*)) clusters were digitised using a 480×512 video digitiser. The microscope magnification was set to ensure that the smallest definable feature of a cluster image covered from one to two pixels. Although individual particles could be resolved easily when viewing the CPM directly in the microscope, this level of detail is lost in the final digitised images. We estimate the microsphere density interior to a cluster to be four per pixel.

The fractal dimension, D_F, is determined from least square fits of the data to the relation, $D_F \log R_G = \log N$, where N is the number of pixels covered by the cluster, and from plots of the pair correlation function, $G(R)$, against distance. The pair correlation function is determined by fitting the relation, $\log G(R) = (D_F - 2) \log R$ to the data, where in all cases R is in pixel units. The method we use to determine D_F from the radius of gyration–mass relation for the extended cluster is essentially that used by Forrest and Witten [5] to analyse smoke particle aggregates; the computer defines a large circle on the digitised image of the aggregate, adjusts its centre to lie on the centre of mass of the circumscribed distribution of occupied pixels, and then calculates the radius of gyration. This process is repeated for a set of nested circles, and D_F is extracted from a least squares fit. The entire exercise is repeated for a series



(*a*) (*b*)

Figure 1. (*a*) Digitised image of a portion of the connected cluster analysed in this letter. The total cluster covered roughly a quarter of the trough surface. (*b*) A digitised image of a distribution of small isolated clusters.

of different initial circles to test for a possible dependence upon origin, and a final average for D_F is found.

Figures 2(*a*) and 2(*b*) are linear and log–log plots, respectively, of the pair correlation function averaged over eleven regions spanning a part of the network cluster. The portion of this cluster covering the digitiser screen contains about 1.5×10^5 microspheres, and $G(R)$ was calculated out to $R=128$ ($R=128$) is the overlap limit of our 256×256 2D FFT) for the eleven regions, each comprising about 1.5×10^4 microspheres. Consequently, the cluster size and the sample sizes used in determining $G(R)$ for the cluster are at least comparable to those employed in the largest 2D simulations.

The plots reveal what seems to be a crossover between two regions of scale invariance. The short-range regime, which persists to about $R\sim20$, yields $D_F=1.42\pm0.03$, in agreement with KCC [2] predictions for the 2D flocculation limit. The long-range regime, $20\leqslant R\leqslant128$, yields $D_F=1.69\pm0.01$; both fractal dimension values are averages over the eleven regions described above and the quoted uncertainties are one standard deviation of the mean. While the latter value of D_F agrees with DLA [6] predictions for 2D, it can probably be connected more sensibly to the value $D_F=1.75\pm0.07$, reported by Kolb and Hermann [7] from a KCC simulation of clustering within the asymptotic time regime near a 2D sol–gel transition. Consistent with this observation, we find $D_F=1.72\pm0.06$ from a fit to the R_G against N data for the giant cluster, using the method of Forrest and Witten mentioned earlier. These data show no evidence of a crossover, but this is to be expected; the long-range data overwhelm the short-range, in the R_G against N fit for the giant cluster.

The crossover is not an artefact of the digitising-analysis process. It remains unchanged under variations in the clipping level, and even under extreme coarse-graining.

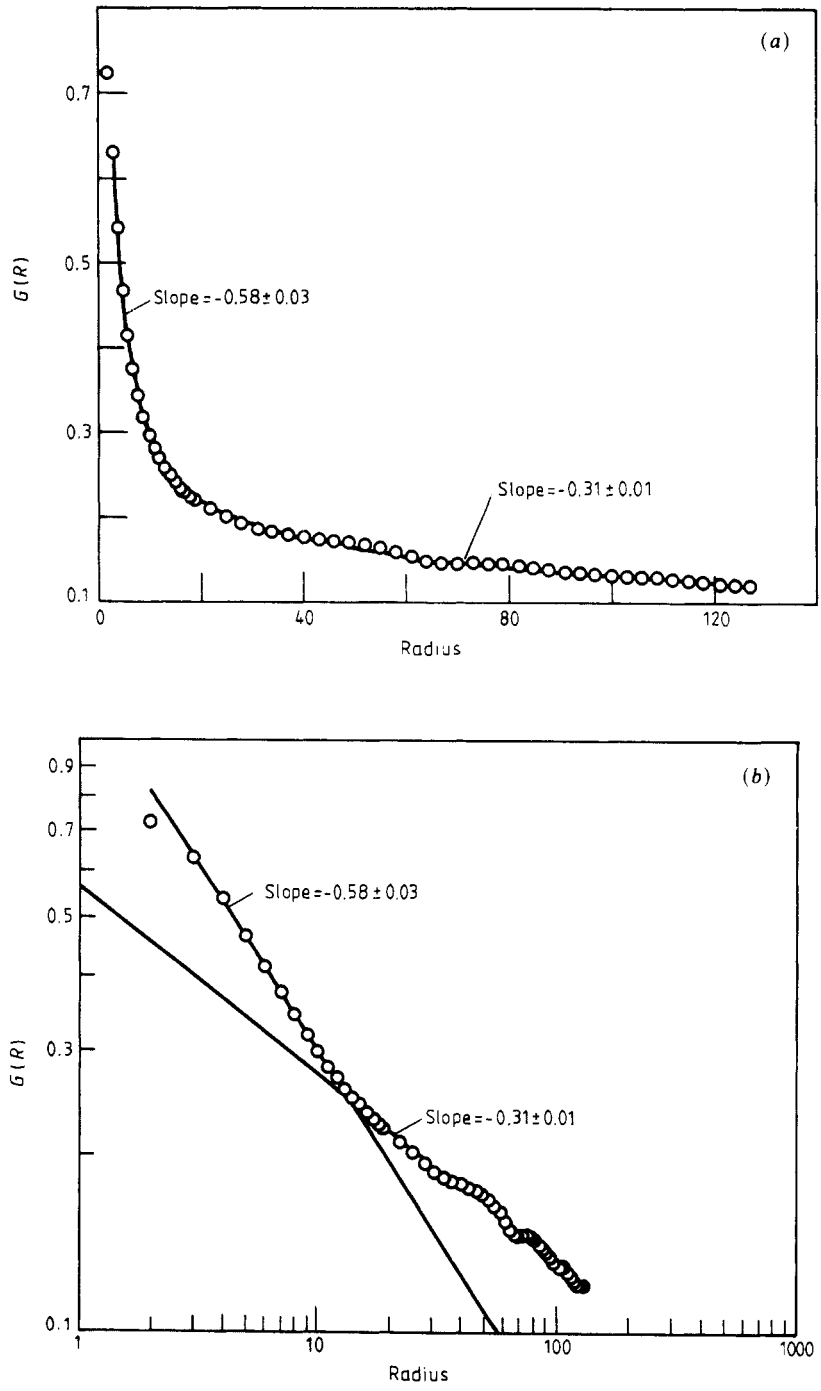


Figure 2. (*a*) and (*b*) are linear and log-log plots, respectively, of the pair correlation function $G(R)$ against R averaged over eleven regions of the connected clusters. The full curves are least square fits to the data. For $R \leqslant 20$, $D_F = 1.42 \pm 0.03$ and $D_F = 1.69 \pm 0.03$ for $20 \leqslant R \leqslant 128$. The value of R corresponding to the dip in $G(R)$ is a measure of the average cluster void size.

We carried out an added test based on the following speculation: if the initial density is sufficiently small, then as suggested by Kolb and Hermann, a crossover may be expected from flocculation to gelation in the *early* stages of cluster formation. If the particle clusters maintain their structural rigidity throughout the aggregation process, the crossover between flocculation and gel-sol regimes should leave its imprint on the $G(R)$ against R record built into the eventual connected cluster. To investigate this possiblity, we identified areas within figure 1(*a*) which seemed to be reasonable choices for contact regions likely to be formed between isolated clusters in the creation of the large aggregate at the gel-sol transition. Then we had the computer break the giant cluster apart at these points into sets of isolated clusters to be considered as hypothetical pre-transition distributions. The average fractal dimension determined from analysis of the pair correlation function dependence upon r for a set of 19 clusters created in this manner, ranging in size from $1500 \leqslant N \leqslant 2100$ pixels, was $D_F = 1.47 \pm 0.02$, compared with the value for the KCC 2D flocculation limit, $D_F = 1.42 \pm 0.05$.

The average fractal dimension derived from fits to plots of log $G(R)$ against log R for the six largest clusters in figure 1(*b*) is $D_F = 1.20 \pm 0.11$, in remarkably good agreement with the value quoted by Hurd and Schaefer which were based on radius of gyration measurements. We also determined D_F from pair correlation measurements made on a photomicrograph of the Hurd-Schaefer clusters, kindly sent to us by Allan Hurd. We find $D_F = 1.24 \pm 0.08$, where the average is over five of their largest clusters, comparable in size (roughly 1500 microspheres, or 400 pixels covered) to those included in our set. In all cases, the straight line portion of the log $G(R)$ against log R plots extended 20 or fewer pixel units (roughly 40 particle diameters for our clusters and 50 for theirs), then fell off in characteristic finite size behaviour. The quoted uncertainties are one standard deviation; individual cluster D_F estimates ranged from 1.15 to 1.38. These results remain stable under variations of the digitiser clipping level which affect the image edge resolution.

Surprisingly, we find $D_F = 1.6 \pm 0.3$ from figure 3, the log plot of R_G against N for the entire cluster distribution of figure 1(*b*), while a comparable plot which includes just the six largest clusters yields $D_F = 1.38 \pm 0.28$. This apparent discrepancy illustrates a possible difficulty with the uncritical use of R_G against mass data from aggregate distributions. The smaller of our clusters appear like 'blobs' rather than fractals, and their $G(R)$ show no scaling behaviour. Yet when included in figure 3 they fit very nicely on what appears to be a power law, the scatter appearing equivalent to that in the comparable Hurd-Schaefer plot. It is possible that this drift toward higher effective dimension with reduced cluster size signals a scale change occurring at the two to three pixel distance range, an indication that short-range electrostatic forces may persist over distances greater than a pixel.

In summary, we found and analysed two classes of clusters which were formed during irreversible aggregation of a 2D distribution of polystyrene microspheres at an air-water interface.

(i) Analyses of $G(R)$ and of the radius of gyration against mass dependence for a large connected cluster yield results which are in essential agreement with predictions made by Kolb and Herrmann [7], based on a KCC simulation of particle aggregation in two dimensions near a gel-sol transition. We also find evidence of a distinct crossover between KCC flocculation and gel-sol scaling regimes which occurs at small R values, or equivalently, at early times in the aggregation process. This suggests that a partial historical record of growth conditions can be recovered from studies of the scaling behaviour of $G(R)$ as a function of cluster size.

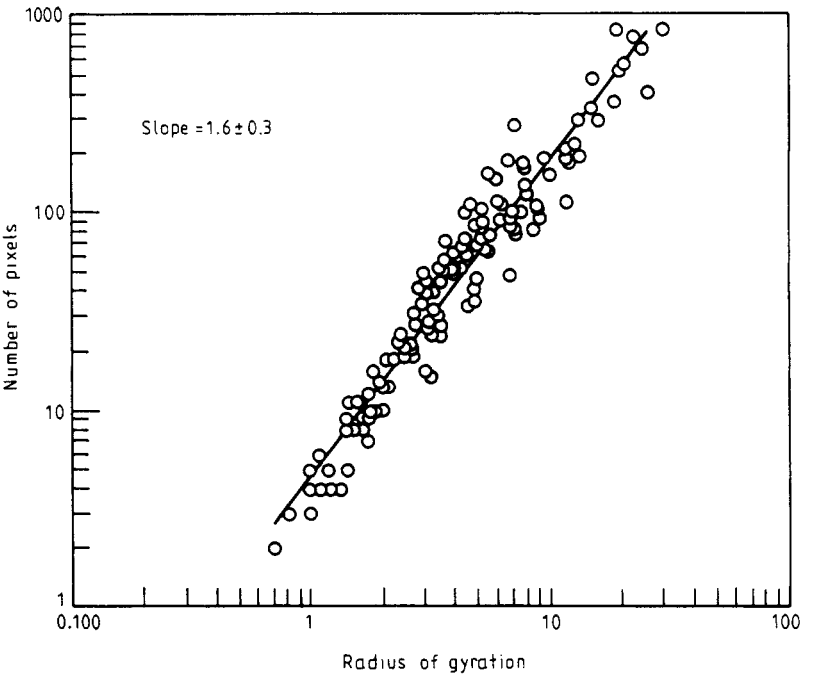


Figure 3. The log of N against log R_G for the distribution of clusters shown in figure 1(b). All clusters covering more than one pixel are included. The full line is a least squares fit to the data, corresponding to $D_F = 1.60 \pm 0.3$. Values as large as $D_F = 1.78$, with an equally good fit, resulted when the digitised portion of the image was adjusted to increase the portion covered by the smaller clusters.

(ii) Isolated clusters, which we speculate grew from a lower density region of the sample, have low values of D_F in excellent agreement with the result quoted by Hurd and Schaefer, and with the value $D_F = 1.26 \pm 0.06$, predicted by Jullien [3] from a 'biased' KCC simulation designed to replicate the effects on aggregation of electrostatic anisotropy. The possibility that the Hurd-Schaefer clusters and ours were formed under similar conditions was supported from measurements we made of the pair correlation functions for five of their largest clusters.

Nevertheless, there are inconsistencies. While the largest of our isolated clusters have small fractal dimensions, the smallest aggregates have a compact, essentially two-dimensional structure. When they were included in the distribution used to determine D_F from a radius of gyration against cluster size analysis, larger D_F values were inferred. The compact appearance of the smallest aggregates is consistent with the existence of a remanent, largely isotropic, repulsive force extending over several pixel units. In any case, our experience suggests that care should be taken when applying radius of gyration analyses to real aggregating systems.

Finally, no evidence for the influence of anisotropic interactions were seen from analyses of the extended aggregate, even at small R values where KCC flocculation-limit scaling seems to prevail. We are carrying out studies of the time evolution of $G(R)$ for clusters and of the cluster size distribution in aggregating CPM, in an effort to address these apparent discrepancies. Aggregation in experimental particle systems may have embedded complexities not built into computer simulations.

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